Fluctuations in the presence of fields: Phenomenological Gaussian approximation and a class of thermodynamic inequalities

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The fluctuations of thermodynamic systems in the presence of the fields are considered. The approach is of phenomenological nature and developed in a Gaussian approximation. The cases of a magnetizable continuum in a magnetoquasistatic field, as well as the so called discrete systems are used to exemplify the study. In the latter case one finds that the fluctuation estimators depend both on the intrinsic properties of the system and on the characteristics of the environment. Following earlier ideas of one of the authors we present a class of thermodynamic inequalities for the systems investigated in this paper. In the case of two variables these inequalities are nonquantum analogs of the well known quantum Heisenberg ''uncertainty'' relations. In this context, the fluctuation estimators support the idea that Boltzmann's constant k has the signification of a generic indicator of stochasticity for thermodynamic systems.

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I. INTRODUCTION

The literature from the last decades promoted some interesting attempts [1–6] in order [4] ''to formulate a comprehensive and unified theory of thermodynamics in the presence of fields.'' These attempts approached the description of the thermodynamic systems only in terms of macroscopic quantities regarded as deterministic variables, unendowed with fluctuations.

On the other hand it is a well established fact that, due to their inner microscopic structure, the thermodynamic systems must be characterized by means of variables endowed with fluctuations. The mean values of the respective variables coincide with macroscopic quantities that characterize ordinary thermodynamics. The alluded fluctuations require description in terms of some additional concepts of probabilistic nature (e.g., dispersions, correlations, higher order moments). Such a description can be done in a phenomenological or in a statistical-mechanics manner. In this paper we try to develop a description of fluctuations specific for thermodynamic systems in the presence of fields. Our description is done in a phenomenological manner. We resort to usual procedures of phenomenological theory [2,4,7,8] and use some ideas inspired by our earlier works on fluctuations [9,10].

We start a search for a first approximation of the generalized distribution of fluctuation probabilities. For this we use the concept of adequate internal energy inspired by Ref. [4]. A first application is focused on the second order moments for the fluctuations in magnetizable continuum in a magnetoquasistatic field. Next we investigate briefly the questions connected with fluctuations in discrete systems in the presence of a magnetic field. By using the results of this investigation we introduce in the next section a class of thermodynamic inequalities, in a manner similar to the one developed in Ref. [9].

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II. GENERAL THEORETICAL CONSIDERATIONS

The phenomenological theory of fluctuations deals with real and continuous variables endowed with an *ad hoc* stochasticity (without any reference to the microscopic structure of the thermodynamic systems). For small fluctuations in the proximity of equilibrium states the corresponding probability density is given [2,7,8] by

$$w \sim \exp\left\{\frac{\delta S'}{k}\right\}, \tag{1}$$

where $\delta S' = S'(x) - S'(\overline{x})$ denotes the deviation of entropy from its mean due to the fluctuations, x signifies the set of macroscopic variables characterizing the system, with $\overline{x}$ being its equilibrium mean (or expectation), and k is Boltzmann's constant. The variation $\delta S'$, which refers to the ensemble of thermodynamic system and its environment is given by

$$\delta S' = -\frac{\delta W_{\min}}{T_{eq}}, \tag{2}$$

where T_{eq}=equilibrium temperature and $\delta W_{\min}$=minimal work of fluctuations.

Note that in Eq. (1) as well as in all subsequent formulas for the probability density w we are omitting the constants that precede the exponential functions. These constants can readily be determined by imposing the normalization condition for w.

Let us focus our attention on systems in the presence of fields (as they are viewed in Refs. [4–6]). We introduce the work $\delta W_{\min}$ through the relation

$$\delta\hat{U} = \sum_r \hat{\xi}_r\, \delta Y_r + \sum_l \Psi_l\, \delta Z_l + \delta W_{\min} \tag{3}$$

with the following notations: δA is the variation (due to the fluctuations) of the variable A; $\hat{U}$ is the internal energy in the presence of fields; $\hat{\xi}_r$ are the field dependent intensive variables (e.g. $\hat{\xi}_1 = T$ is the temperature, while $-\hat{\xi}_2 = \hat{p}$ and $\hat{\xi}_3 = \hat{\zeta}$ denote the field dependent pressure and chemical potential); Y_r is the conventional extensive thermodynamic variables (e.g., entropy S, volume V, number of particles N); Ψ_l and Z_l denote the additional parameters due to the presence of fields (e.g., $\Psi = V\mathbf{H}$, $Z = \mathbf{B}$ for the case of magnetic fields of strength $\mathbf{H}$ and induction $\mathbf{B}$).

Note that generally the quantities Ψ_l are not intensive conjugates of Z_l.

In Eq. (3) $\hat{U}$ depends on Y_r and Z_l, so that its total differential is given by

$$d\hat{U} = \sum_r \hat{\xi}_r \, dY_r + \sum_l \Psi_l \, dZ_l . \tag{4}$$

For the sake of brevity we introduce the following compacted notation $\{Y_r\} \cup \{Z_l\} =_{def} \{\eta_i\}$ and $\{\hat{\xi}_r\} \cup \{\Psi_l\} \overset{def}{=} \{\Phi i\}$. Hence, in accordance with Eq. (4),

$$\Phi_i = \left(\frac{\partial \hat{U}}{\partial \eta_i} \right)_{eq} , \tag{5}$$

where the index eq denotes the equilibrium value of the indexed quantity.

The second order approximation of $\delta\hat{U}$ in terms of the variations $\delta\eta_i$ can be written as

$$\begin{aligned} \delta\hat{U} &= \sum_i \left(\frac{\partial \hat{U}}{\partial \eta_i} \right)_{eq} \delta\eta_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \hat{U}}{\partial \eta_i \, \partial \eta_j} \right)_{eq} \delta\eta_i \, \delta\eta_j \\ &= \sum_i \Phi_i \, \delta\eta_i + \frac{1}{2} \sum_i \left(\sum_j \frac{\partial \Phi_i}{\partial \eta_j} \delta\eta_j \right) \delta\eta_i \\ &= \sum_i \Phi_i \, \delta\eta_i + \frac{1}{2} \sum_i \delta\Phi_i \, \delta\eta_i . \end{aligned} \tag{6}$$

Using the relations (2)–(6) in conjunction with Eq. (1), one obtains

$$w \sim \exp\left\{ -\frac{1}{2kT} \sum_i \delta\Phi_i \, \delta\eta_i \right\} . \tag{7}$$

In this relation as well as in all the subsequent ones we symbolize the equilibrium temperature simply with T [instead of T_{eq} used in Eq. (2)].

For a given system, due to their physical nature, the variables from the sets $\{\Phi i\}$ and $\{\eta_i\}$ are generally interdependent. However one can always select instead a restrictive set of physically independent variables $\{X_a\}_{a=1}^{n}$. This transcribes Eq. (7) into the following multivariable Gaussian distribution,

$$w \sim \exp\left\{ -\frac{1}{2} \sum_{a=1}^{n} \sum_{b=1}^{n} \alpha_{ab} \, \delta X_a \, \delta X_b \right\} , \tag{8}$$

where

$$\alpha_{ab} = \frac{1}{kT} \sum_j \left(\frac{\partial \Phi_j}{\partial X_a} \right)_{eq} \left(\frac{\partial \eta_j}{\partial X_b} \right)_{eq} \tag{9}$$

can be identified as the field dependent elements of a matrix α.

Note that in the Gaussian distribution (8) the quantities $\{X_a\}$ are considered as continuous variables, in the range $(-\infty,\infty)$.

The variables $\{X_a\}$ used in Eq. (8) are characterized by the correlations

$$C_{ab} = \overline{\delta X_a \, \delta X_b} = (\alpha^{-1})_{ab} . \tag{10}$$

Here $(\alpha^{-1})_{ab}$ denote the elements of the inverse matrix of α given by Eq. (9), while the over bar in $\overline{F}$ signifies the expectation value of the quantity F defined as

$$\overline{F} = \int F(\{X_a\}) w(\{X_a\}) \prod_b dX_b .$$

For any set of quantities $\{Q_m\}$ expressible in terms of independent variables $\{X_a\}$ [i.e., $Q_m = Q_m(X_a)$] the fluctuations are characterized by the correlations

$$C_{ms} = \sum_a \sum_b \left(\frac{\partial Q_m}{\partial X_a} \right)_{eq} \left(\frac{\partial Q_s}{\partial X_b} \right)_{eq} (\alpha^{-1})_{ab} . \tag{11}$$

If $m = s$ then the correlation $C_{mm} = \mathcal{D}_m$ denote just the dispersion of fluctuations for the quantity Q_m.

As in the case of fluctuations in the absence of fields [9] the correlations (11) constitute a real, symmetric and non-negative definite matrix. Hence,

$$\det\left[\sum_a \sum_b \left(\frac{\partial Q_m}{\partial X_a} \right)_{eq} \left(\frac{\partial Q_s}{\partial X_b} \right)_{eq} (\alpha^{-1})_{ab} \right] \geqslant 0. \tag{12}$$

Application of the above description for fluctuations in the presence of fields requires the following steps.

(1) To establish the adequate expression (4) for the total differential $d\hat{U}$ of the internal energy (to this end the results from [4–6] are highly recommendable).

(2) To evaluate the minimal work $\delta W_{\min}$ of fluctuations by using Eq. (3).

(3) To identify the set of the independent variables $\{X_a\}$.

(4) To account for the adequate equations of state and thermodynamic Maxwell relations (e.g., such as those given by [2,5–8]).

(5) To compute the correlations C_{ms} through relation (10) or (11).

(6) To formulate relevant field dependent thermodynamic inequalities by using Eq. (12).

Evaluation of correlations and thermodynamic inequalities are discussed in the following sections.

III. EVALUATION OF SOME CORRELATIONS

A. Magnetizable continuum in the presence of magnetoquasistatic field

We assume that all the magnetic energy is stored uniformly within the boundaries of the system. The adequate expression of the internal energy differential, as in [4], has the form

$$d\hat{U}=T\,dS-\hat{p}\,dV+\hat{\zeta}\,dN+V\mathbf{H}\cdot d\mathbf{B} \tag{13}$$

In this relation, as well as in the subsequent ones, the implied symbols for physical variables signify the mean values corresponding to an equilibrium state. The quantities $\hat{p}$ and $\hat{\zeta}$ are intensive parameters that are dependent on the field. These parameters have [4–6] various expressions, depending on the physical constraints of the system.

The minimal work of the fluctuations can be expressed as

$$\delta W_{\mathrm{min}}=\delta\hat{U}-T\,\delta S+\hat{p}\,\delta V-\hat{\zeta}\,\delta N-V\mathbf{H}\cdot\delta\mathbf{B} \tag{14}$$

As independent variables we take T, V, N, and $\mathbf{B}$. Their independence must be regarded in a thermodynamic sense, because they can be interdependent from a statistical approach.

For the probability density (8) one obtains

$$\begin{aligned} w\sim\exp\Bigg\{-\frac{1}{2kT}\Bigg[&\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}(\delta T)^2-\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}(\delta V)^2\\ &+\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}(\delta N)^2+V\left(\frac{\partial\mathbf{H}}{\partial\mathbf{B}}\right)_{T,V,N}(\delta B)^2\\ &+2\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}}\delta V\,\delta N+2\left(\frac{\partial(V\mathbf{H})}{\partial V}\right)_{T,N,\mathbf{B}}\delta V\cdot\delta\mathbf{B}\\ &+2V\left(\frac{\partial\mathbf{H}}{\partial N}\right)_{T,V,\mathbf{B}}\delta N\cdot\delta\mathbf{B}\Bigg]\Bigg\} \end{aligned} \tag{15}$$

For details see the Appendix.

The matrix of the correlation coefficients is

$$(\alpha)=\begin{pmatrix}\alpha_{11}&0&0&0\\0&\alpha_{22}&\alpha_{23}&\alpha_{24}\\0&\alpha_{32}&\alpha_{33}&\alpha_{34}\\0&\alpha_{42}&\alpha_{43}&\alpha_{44}\end{pmatrix}, \tag{16}$$

where

$$\alpha_{11}=\frac{1}{kT}\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}};\quad \alpha_{22}=-\frac{1}{kT}\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}};$$

$$\alpha_{33}=\frac{1}{kT}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}};\quad \alpha_{44}=\frac{V}{kT}\left(\frac{\partial\mathbf{H}}{\partial\mathbf{B}}\right)_{T,V.N}=\frac{V}{kT\mu};$$

$$\alpha_{12}=\alpha_{21}=0;\quad \alpha_{13}=\alpha_{31}=0;\quad \alpha_{14}=\alpha_{41}=0;$$

$$\alpha_{23}=\alpha_{32}=\frac{1}{kT}\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}};$$

$$\alpha_{24}=\alpha_{42}=\frac{1}{kT}\left(\frac{\partial(V\mathbf{H})}{\partial V}\right)_{T,N,\mathbf{B}}=\frac{\mathbf{H}}{kT}\left[1+\frac{\rho}{\mu}\left(\frac{\partial\mu}{\partial\rho}\right)_T\right];$$

$$\alpha_{34}=\alpha_{43}=\frac{V}{kT}\left(\frac{\partial\mathbf{H}}{\partial N}\right)_{T,V,\mathbf{B}}=-\frac{\mathbf{H}}{kT\mu}\left(\frac{\partial\mu}{\partial\rho}\right)_T.$$

In the above relations ρ is particles per unit volume ($\rho=N/V$) and μ denotes the magnetic permeability of the system.

Thus the dispersions and correlations are obtained as

$$\overline{(\delta T)^2}=(\alpha^{-1})_{11}=\frac{1}{\alpha_{11}}, \tag{17}$$

$$\overline{(\delta V)^2}=(\alpha^{-1})_{22}=\frac{\begin{vmatrix}\alpha_{33}&\alpha_{34}\\\alpha_{34}&\alpha_{44}\end{vmatrix}}{\det|\beta|}, \tag{18}$$

$$\overline{(\delta N)^2}=(\alpha^{-1})_{33}=\frac{\begin{vmatrix}\alpha_{22}&\alpha_{24}\\\alpha_{24}&\alpha_{44}\end{vmatrix}}{\det|\beta|}, \tag{19}$$

$$\overline{(\delta B)^2}=(\alpha^{-1})_{44}=\frac{\begin{vmatrix}\alpha_{22}&\alpha_{23}\\\alpha_{23}&\alpha_{33}\end{vmatrix}}{\det|\beta|}, \tag{20}$$

$$\overline{\delta T\;\delta V}=\overline{\delta T\;\delta N}=\overline{\delta T\;\delta\mathbf{B}}=0, \tag{21}$$

$$\overline{\delta V\;\delta N}=(\alpha^{-1})_{23}=-\frac{\begin{vmatrix}\alpha_{23}&\alpha_{34}\\\alpha_{24}&\alpha_{44}\end{vmatrix}}{\det|\beta|}, \tag{22}$$

$$\overline{\delta V\;\delta\mathbf{B}}=(\alpha^{-1})_{24}=\frac{\begin{vmatrix}\alpha_{23}&\alpha_{33}\\\alpha_{24}&\alpha_{34}\end{vmatrix}}{\det|\beta|}, \tag{23}$$

$$\overline{\delta N\;\delta\mathbf{B}}=(\alpha^{-1})_{34}=-\frac{\begin{vmatrix}\alpha_{22}&\alpha_{23}\\\alpha_{24}&\alpha_{34}\end{vmatrix}}{\det|\beta|}, \tag{24}$$

where

$$\det|\beta|=\begin{vmatrix}\alpha_{22}&\alpha_{23}&\alpha_{24}\\\alpha_{23}&\alpha_{33}&\alpha_{34}\\\alpha_{24}&\alpha_{34}&\alpha_{44}\end{vmatrix}. \tag{25}$$

Let us focus on some particular cases.

1. V=const, N=const

In this case the matrix α is of the form

$$(\alpha)=\begin{pmatrix}\alpha_{11} & 0\\ 0 & \alpha_{22}\end{pmatrix} \tag{26}$$

with

$$\alpha_{11}=\frac{1}{kT}\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}};\quad \alpha_{22}=\frac{V}{kT}\left(\frac{\partial \mathbf{H}}{\partial \mathbf{B}}\right)_{V,N,T}.$$

The entropy of the system in the presence of the magnetic field is given by [1,3,5]

$$S=S_0+\frac{1}{2}VH^2\left(\frac{\partial \mu}{\partial T}\right)_{\rho}, \tag{27}$$

where S_0 denotes the entropy in the absence of the field.

In this case the expressions for the dispersions and correlations of various physical variables are

$$\overline{(\delta T)^2}=(\alpha^{-1})_{11}=\frac{kT}{\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}}=\frac{kT^2}{C_V+\frac{1}{2}TVH^2\left[\left(\frac{\partial^2\mu}{\partial T^2}\right)_{\rho}-\frac{2}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_{\rho}^2\right]}, \tag{28}$$

$$\overline{(\delta B)^2}=(\alpha^{-1})_{22}=\frac{kT}{V\left(\frac{\partial \mathbf{H}}{\partial \mathbf{B}}\right)_{V,N,T}}=\frac{kT\mu}{V}, \tag{29}$$

$$\overline{\delta T\,\delta B}=0, \tag{30}$$

$$\overline{\delta T\,\delta S}=\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}\overline{(\delta T)^2}=kT, \tag{31}$$

$$\overline{\delta T\,\delta \mathbf{H}}=\left(\frac{\partial \mathbf{H}}{\partial T}\right)_{V,N,\mathbf{B}}\overline{(\delta T)^2}=-\frac{\mathbf{H}}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_{\rho}\frac{kT^2}{C_V+\frac{1}{2}TVH^2\left[\left(\frac{\partial^2\mu}{\partial T^2}\right)_{\rho}-\frac{2}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_{\rho}^2\right]}, \tag{32}$$

$$\overline{\delta \mathbf{B}\cdot\delta \mathbf{H}}=\left(\frac{\partial \mathbf{H}}{\partial \mathbf{B}}\right)_{V,N,T}\overline{(\delta B)^2}=\frac{kT}{V}, \tag{33}$$

$$\overline{\delta S\,\delta \mathbf{B}}=\left(\frac{\partial S}{\partial \mathbf{B}}\right)_{V,N,T}\overline{(\delta B)^2}=kT\mathbf{H}\left(\frac{\partial\mu}{\partial T}\right)_{\rho}. \tag{34}$$

Here C_V denotes the isochoric heat capacity: $C_V=T(\partial S_0/\partial T)_{V,N}$. In the absence of the field $\overline{(\delta T)^2}$ as given by Eq. (28) reduces to the previously known expression [7–9].

2. B=const

This case is associated with a constant magnetic induction. The quantities T, V, and N are regarded as random variables (i.e., endowed with fluctuations).

In this case, according to Ref. [4], one can write

$$d\hat{U}=TdS-\hat{p}dV+\hat{\zeta}dN, \tag{35}$$

where

$$\hat{p}=p_{\mathbf{B},N}=p-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}-\frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_T, \tag{36}$$

$$\hat{\zeta}=\zeta_{\mathbf{B},V}=\zeta-\frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_T, \tag{37}$$

while p and ζ denote, respectively, the pressure and chemical potential in the absence of the field.

The matrix of the correlation coefficients has the form

$$(\alpha)=\begin{pmatrix}\alpha_{11} & 0 & 0\\ 0 & \alpha_{22} & \alpha_{23}\\ 0 & \alpha_{23} & \alpha_{33}\end{pmatrix}. \tag{38}$$

Using Eq. (11) and some uncomplicated algebraic operations one finds

$$\overline{(\delta T)^2}=(\alpha^{-1})_{11}=\frac{kT}{\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}}, \tag{39}$$

$$\overline{(\delta V)^2}=(\alpha^{-1})_{22}=\frac{\alpha_{33}}{\alpha_{22}\alpha_{33}-\alpha_{23}^2}=-kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}}{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}+\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}}^2}, \tag{40}$$

$$\overline{(\delta N)^2}=(\alpha^{-1})_{33}=\frac{\alpha_{22}}{\alpha_{22}\alpha_{33}-\alpha_{23}^2}=kT\frac{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}}{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}+\left(\frac{\partial\hat{\zeta}}{\partial V}\right)^2_{T,N,\mathbf{B}}},\tag{41}$$

$$\overline{\delta V\,\delta N}=(\alpha^{-1})_{23}=\frac{\alpha_{23}}{\alpha_{23}^2-\alpha_{22}\alpha_{33}}=kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}}}{\left(\frac{\partial\hat{\zeta}}{\partial V}\right)^2_{T,N,\mathbf{B}}+\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}},\tag{42}$$

$$\overline{\delta T\,\delta V}=0;\overline{\delta T\,\delta N}=0.\tag{43}$$

Equations (39)–(42) imply the following relations.

$$\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}=\frac{C_V}{T}+\frac{1}{2}VH^2\left[\left(\frac{\partial^2\mu}{\partial T^2}\right)_\rho-\frac{2}{\mu}\left(\frac{\partial\mu}{\partial T}\right)^2_\rho\right],\tag{44}$$

$$\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}=\left(\frac{\partial\zeta}{\partial N}\right)_{T,V}+\frac{H^2}{\mu V}\left(\frac{\partial\mu}{\partial\rho}\right)^2_T-\frac{1}{2}\frac{H^2}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T,\tag{45}$$

$$\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}=\left(\frac{\partial p}{\partial V}\right)_{T,N}-\frac{H^2\rho^2}{\mu V}\left(\frac{\partial\mu}{\partial\rho}\right)^2_T+\frac{1}{2}\frac{H^2\rho^2}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T,\tag{46}$$

$$\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}}=\left(\frac{\partial\zeta}{\partial V}\right)_{T,N}-\frac{H^2\rho}{\mu V}\left(\frac{\partial\mu}{\partial\rho}\right)^2_T+\frac{1}{2}\frac{H^2\rho}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T.\tag{47}$$

3. $\mathbf{H}$=const

In this case the current densities (the sources of the magnetic field) are constant. We search the parameters of fluctuations for the quantities T, V, and N.

The differential of the internal energy is given by Eq. (13) where according to Ref. [4]

$$\hat{p}=p_{\mathbf{H},N}=p-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}+\frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_T,\tag{48}$$

$$\hat{\zeta}=\zeta_{\mathbf{H},V}=\zeta+\frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_T.\tag{49}$$

In this case, as proved in [6], the entropy is

$$S(\mathbf{H}=\text{const})=S_0-\frac{1}{2}VH^2\left(\frac{\partial\mu}{\partial T}\right)_\rho.\tag{50}$$

Using this expression for the entropy one obtains,

$$\overline{(\delta T)^2}=\frac{kT}{\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{H}}}=\frac{kT^2}{C_V-\frac{1}{2}TVH^2\left(\frac{\partial^2\mu}{\partial T^2}\right)_\rho},\tag{51}$$

$$\overline{(\delta V)^2}=-kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{H}}}{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{H}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{H}}+\left(\frac{\partial\hat{\zeta}}{\partial V}\right)^2_{T,N,\mathbf{H}}},\tag{52}$$

$$\overline{(\delta N)^2}=kT\frac{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{H}}}{\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{H}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{H}}+\left(\frac{\partial\hat{\zeta}}{\partial V}\right)^2_{T,N,\mathbf{H}}},\tag{53}$$

$$\overline{\delta V\,\delta N}=kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{H}}}{\left(\frac{\partial\hat{\zeta}}{\partial V}\right)^2_{T,N,\mathbf{H}}+\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{H}}\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{H}}},\tag{54}$$

where

$$\left(\frac{\partial\hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{H}}=\left(\frac{\partial\zeta}{\partial N}\right)_{T,V}+\frac{1}{2}\frac{H^2}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T,\tag{55}$$

$$\left(\frac{\partial\hat{p}}{\partial V}\right)_{T,N,\mathbf{H}}=\left(\frac{\partial p}{\partial V}\right)_{T,N}-\frac{1}{2}\frac{H^2\rho^2}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T,\tag{56}$$

$$\left(\frac{\partial\hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{H}}=\left(\frac{\partial\zeta}{\partial V}\right)_{T,N}-\frac{1}{2}\frac{H^2\rho}{V}\left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T.\tag{57}$$

Note that

(1) all the above relations refer to the case of linear magnetic materials, for which μ, being independent of H, depends only on the temperature T and particle number density ρ;

(2) for practical purposes it is more useful to evaluate the fluctuation of the magnetization $\mathbf{M}$ rather than that of the magnetic induction. This can be done by introducing the function

$$\hat{U}^*=\hat{U}-\frac{1}{2}V\mu_0H^2,\tag{58}$$

and provided the change of H due to the presence of the magnetic system can be neglected. Rigorously, one must substract from $\hat{U}$ the quantity $\frac{1}{2}V\mu_0\mathcal{H}^2$, where $\mathcal{H}$ is the field strength generated in free space by the sources , in absence of the system (for similar considerations see Ref. [1]). For most linear systems the magnetic susceptibility has a low value. Therefore the deformation of the field due to the system presence can be neglected. In such a case one obtains,

$$d\hat{U}^* = TdS - \hat{p}dV + \hat{\zeta}dN + V\mathbf{H}\cdot d(\mu_0\mathbf{M}), \tag{59}$$

where

$$\mathbf{M} = \chi_m \mathbf{H}, \tag{60}$$

$$\hat{p} = p - \frac{1}{2}\mu_0\mathbf{H}\cdot\mathbf{M} - \frac{1}{2}H^2\rho\mu_0\frac{\partial\chi_m}{\partial\rho}, \tag{61}$$

$$\hat{\zeta} = \zeta - \frac{1}{2}H^2\mu_0\frac{\partial\chi_m}{\partial\rho}. \tag{62}$$

In the last three relations μ_0 and χ_m denote magnetic permeability of free space and magnetic susceptibility, respectively.

If V and N are fixed, then one finds the following known relation [2],

$$\overline{(\delta M)^2} = \frac{kT\mu_0\chi_m}{V}. \tag{63}$$

(3) In the case of a dielectric continuum the corresponding expressions of the fluctuations can be obtained by means of the following substitutions: $\mathbf{B}\to\mathbf{D}$; $\mathbf{H}\to\mathbf{E}$; $\mu\to\varepsilon$, where $\mathbf{D}$ is the electric displacement, $\mathbf{E}$ is the electric field strength and ε denotes permittivity. In this context $\mu_0\mathbf{M}$ must to be replaced with $\mathbf{P}$ (electric polarization) and χ_m with χ_e (electric susceptibility).

(4) It is easy to observe that the dispersions $\overline{(\delta A)^2}$ and correlations $\overline{\delta A\ \delta B}$ from the above established formulas appear as products of Boltzmann's constant k with expressions that contain exclusively mean values of the random variables. It should be noted that the respective values identify themselves with the variables from ordinary (nonstochastic) thermodynamics.

B. The case of discrete systems

Discrete systems are characterized by the fact that the field lines extend beyond their boundaries. Consequently the field energy is stored inside as well as outside the system. These systems should be investigated regarding the effect of fluctuations (i.e., an evaluation of their stochastic characteristics). In the following we consider a particular case investigated by Zimmels [5]. This case involves a sphere of radius R placed in an external uniform magnetic field of strength $\mathbf{H}_0$.

The generalized internal energy of the sphere can be expressed as,

$$dU_1 = TdS_1 - \hat{p}dV_1 + \hat{\zeta}dN_1 + \psi dB_1, \tag{64}$$

where the following relations were taken from [5]:

$$\psi = V_1\frac{B_1}{\mu_s'} = V_1H_1\sqrt{\frac{\mu_s}{\mu_s'}}, \tag{65}$$

$$\mu_s = \frac{\mu_1}{9}\left(\frac{\mu_1}{\mu_2} - 2\frac{\mu_2}{\mu_1} + 1\right), \tag{66}$$

$$\frac{1}{\mu_s'} = \frac{1}{9}\left(\frac{1}{\mu_2} + \frac{1}{\mu_1} - 2\frac{\mu_2}{\mu_1^2}\right). \tag{67}$$

In the above relations as well as in the following ones the indexes 1 and 2 refer to the system (sphere) and its surroundings, respectively.

Let us now discuss some particular situations.

1. V_1=const, N_1=const

In this situation the entropy of the sphere, as given in [5], is

$$S_1 = S_{01} + \frac{1}{18}V_1B_1^2\left[\alpha\frac{\partial\mu_2}{\partial T} - \beta\frac{\partial\mu_1}{\partial T}\right], \tag{68}$$

where S_{01} denotes the entropy in the absence of the field and

$$\alpha = \frac{1}{\mu_2^2} + \frac{2}{\mu_1^2}; \quad \beta = \frac{4\mu_2}{\mu_1^3} - \frac{1}{\mu_1^2}. \tag{69}$$

Note that relations (65)–(69) refer to a state of equilibrium.

Selecting the quantities T and B_1 as independent variables, one obtains for their fluctuations:

$$\begin{aligned}\overline{(\delta T)^2} &= \frac{kT}{\left(\frac{\partial S_1}{\partial T}\right)_{V_1,N_1,\mathbf{B}_1}} \\ &= kT^2\Bigg\{C_V + \frac{1}{18}TV_1B_1^2\Bigg[\alpha\frac{\partial^2\mu_2}{\partial T^2} - \beta\frac{\partial^2\mu_1}{\partial T^2} \\ &\quad + \frac{2}{\mu_1^3}\left(\frac{\partial\mu_1}{\partial T}\right)^2\left(\frac{6\mu_2}{\mu_1} - 1\right) \\ &\quad - \frac{2}{\mu_2^3}\left(\frac{\partial\mu_2}{\partial T}\right)^2 - \frac{8}{\mu_1^3}\frac{\partial\mu_1}{\partial T}\frac{\partial\mu_2}{\partial T}\Bigg]\Bigg\}^{-1}\end{aligned} \tag{70}$$

$$\overline{(\delta B_1)^2} = \frac{kT\mu_s'}{V_1} = \frac{kT}{V_1}\left\{\frac{1}{9}\left(\frac{1}{\mu_2} + \frac{1}{\mu_1} - 2\frac{\mu_2}{\mu_1^2}\right)\right\}^{-1}. \tag{71}$$

These relations show that the fluctuations of the macroscopic parameters depend on permeabilities of both the discrete system and its surroundings.

2. B_1=const

In this situation [5] we have

$$dU_1 = TdS_1 - \hat{p}dV_1 + \hat{\zeta}dN_1 \tag{72}$$

with

$$\hat{p} = p_{\mathbf{B}_1,N_1} = p - \frac{B_1^2}{2\mu_s'} + \frac{B_1^2}{18}\left[\alpha\rho_2\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2} + \beta\rho_1\frac{\partial\mu_1}{\partial\rho_1}\right] \tag{73}$$

and

$$\hat{\zeta} = \zeta_{\mathbf{B}_1,V_1} = \zeta + \frac{B_1^2}{18}\left[\frac{V_1}{V_2}\alpha\frac{\partial\mu_2}{\partial\rho_2} + \beta\frac{\partial\mu_1}{\partial\rho_1}\right]. \tag{74}$$

It follows that one obtains for $\overline{(\delta T)^2}$ the same expression as in the previous situation, because the entropy is given by Eq. (68).

The dispersions of V_1 and N_1 are,

$$\overline{(\delta V_1)^2} = -kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{B}_1}}{\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{B}_1}\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{B}_1} + \left(\frac{\partial\hat{\zeta}}{\partial V_1}\right)^2_{T,N_1,\mathbf{B}_1}}, \tag{75}$$

$$\overline{(\delta N_1)^2} = kT\frac{\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{B}_1}}{\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{B}_1}\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{B}_1} + \left(\frac{\partial\hat{\zeta}}{\partial V_1}\right)^2_{T,N_1,\mathbf{B}_1}}. \tag{76}$$

These expressions are only in a formal analogy with the corresponding ones for magnetizable continuum, because they imply specific particularities through the following partial derivatives.

$$\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{B}_1} = \left(\frac{\partial p}{\partial V_1}\right)_{T,N_1} + \frac{B_1^2}{18}\left[\frac{\alpha\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2} + \frac{\beta\rho_1}{V_1}\frac{\partial\mu_1}{\partial\rho_1} + \frac{\partial}{\partial V_1}\left(\alpha\rho_2\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2} + \beta\rho_1\frac{\partial\mu_1}{\partial\rho_1}\right)\right] \tag{77}$$

$$\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{B}_1} = \left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1} + \frac{B_1^2}{18}\frac{\partial}{\partial N_1}\left(\frac{V_1}{V_2}\alpha\frac{\partial\mu_2}{\partial\rho_2} + \beta\frac{\partial\mu_1}{\partial\rho_1}\right), \tag{78}$$

$$\left(\frac{\partial\hat{\zeta}}{\partial V_1}\right)_{T,N_1,\mathbf{B}_1} = \left(\frac{\partial\zeta}{\partial V_1}\right)_{T,N_1} + \frac{B_1^2}{18}\frac{\partial}{\partial V_1}\left(\frac{V_1}{V_2}\alpha\frac{\partial\mu_2}{\partial\rho_2} + \beta\frac{\partial\mu_1}{\partial\rho_1}\right). \tag{79}$$

3. H_1=const

Using the quantities defined in [5] we get the following expressions:

$$\hat{p} = p_{\mathbf{H}_1,N_1} = p - \frac{1}{2}H_1^2\mu_s + \frac{H_1^2}{18}\left(\beta'\rho_1\frac{\partial\mu_1}{\partial\rho_1} + \alpha'\rho_2\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right), \tag{80}$$

$$\hat{\zeta} = \zeta_{\mathbf{H}_1,V_1} = \zeta + \frac{H_1^2}{18}\left(\beta'\frac{\partial\mu_1}{\partial\rho_1} + \alpha'\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right), \tag{81}$$

$$\alpha' = \frac{\mu_1^2}{\mu_2^2} + 2; \quad \beta' = \frac{2\mu_1}{\mu_2} + 1, \tag{82}$$

$$S_1(\mathbf{H}_1 = \text{const}) = S_{01} + \frac{1}{18}V_1H_1^2\left(-\beta'\frac{\partial\mu_1}{\partial T} + \alpha'\frac{\partial\mu_2}{\partial T}\right). \tag{83}$$

Here the fluctuation of the temperature take the following form:

$$\overline{(\delta T)^2} = \frac{kT}{\left(\frac{\partial S}{\partial T}\right)_{V_1,N_1,\mathbf{H}_1}} = kT^2\left\{C_V + \frac{1}{18}TV_1H_1^2\left[\alpha'\frac{\partial^2\mu_2}{\partial T^2} - \beta'\frac{\partial^2\mu_1}{\partial T^2} - \frac{2}{\mu_2}\left(\frac{\partial\mu_1}{\partial T}\right)^2 - \frac{2\mu_1^2}{\mu_2^3}\left(\frac{\partial\mu_2}{\partial T}\right)^2 + \frac{4\mu_1}{\mu_2^2}\frac{\partial\mu_1}{\partial T}\frac{\partial\mu_2}{\partial T}\right]\right\}^{-1}. \tag{84}$$

Correspondingly we find for the fluctuation of V_1 and N_1:

$$\overline{(\delta V_1)^2} = -kT\frac{\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{H}_1}}{\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{H}_1}\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{H}_1} + \left(\frac{\partial\hat{\zeta}}{\partial V_1}\right)^2_{T,N_1,\mathbf{H}_1}}, \tag{85}$$

$$\overline{(\delta N_1)^2} = kT\frac{\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{H}_1}}{\left(\frac{\partial\hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{H}_1}\left(\frac{\partial\hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{H}_1} + \left(\frac{\partial\hat{\zeta}}{\partial V_1}\right)^2_{T,N_1,\mathbf{H}_1}}, \tag{86}$$

where

$$\left(\frac{\partial \hat{p}}{\partial V_1}\right)_{T,N_1,\mathbf{H}_1}=\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}+\frac{H_1^2}{18}\left[\frac{\alpha'\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2}+\beta'\frac{\rho_1}{V_1}\frac{\partial\mu_1}{\partial\rho_1}+\frac{\partial}{\partial V_1}\left(\beta'\rho_1\frac{\partial\mu_1}{\partial\rho_1}+\alpha'\rho_2\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right)\right] \quad (87)$$

$$\left(\frac{\partial \hat{\zeta}}{\partial N_1}\right)_{T,V_1,\mathbf{H}_1}=\left(\frac{\partial \zeta}{\partial N_1}\right)_{T,V_1}+\frac{H_1^2}{18}\frac{\partial}{\partial N_1}\left(\beta'\frac{\partial\mu_1}{\partial\rho_1}+\alpha'\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right), \quad (88)$$

$$\left(\frac{\partial \hat{\zeta}}{\partial V_1}\right)_{T,N_1,\mathbf{H}_1}=\left(\frac{\partial \zeta}{\partial V_1}\right)_{T,N_1}+\frac{H_1^2}{18}\frac{\partial}{\partial V_1}\left(\beta'\frac{\partial\mu_1}{\partial\rho_1}+\alpha'\frac{V_1}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right). \quad (89)$$

It is interesting at this point to discuss the extreme case of infinite permeability of the sphere, $\mu_2/\mu_1\to 0$, where the field energy is stored exclusively outside its boundaries. In this case

$$\alpha=\frac{1}{\mu_2^2};\quad \beta=0;\quad H_1=0;$$

$$\lim_{\mu_1\to\infty} B_1=3\mu_2H_0;\quad \mu_s'=9\mu_2. \quad (90)$$

If V_1 and N_1 are fixed then

$$\overline{(\delta T)^2}=kT^2\left\{C_V+\frac{1}{2}TV_1H_0^2\left[\frac{\partial^2\mu_2}{\partial T^2}-\frac{2}{\mu_2}\left(\frac{\partial\mu_2}{\partial T}\right)^2\right]\right\}^{-1}, \quad (91)$$

$$\overline{(\delta B_1)^2}=\frac{9kT\mu_2}{V_1}. \quad (92)$$

If $\mathbf{B}_1=$const and $V_1\ll V_2$ then $\hat{p}$ and $\hat{\zeta}$ reduce to the following expressions

$$\hat{p}=p-\frac{\mu_2H_0^2}{2}=p-\frac{1}{18}\frac{B_1^2}{\mu_2}, \quad (93)$$

$$\hat{\zeta}=\zeta \quad (94)$$

given in Ref. [5].

The fluctuations of V_1 and N_1 are characterized by the dispersions:

$$\overline{(\delta V_1)^2}=-kT\frac{\left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1}}{\left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1}\left[\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}+\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right]+\left(\frac{\partial\zeta}{\partial V_1}\right)_{T,N_1}^2}, \quad (95)$$

$$\overline{(\delta N_1)^2}=kT\frac{\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}+\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2}}{\left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1}\left[\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}+\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right]+\left(\frac{\partial\zeta}{\partial V_1}\right)_{T,N_1}^2}. \quad (96)$$

In the same extreme case at $\mathbf{H}_1=$const we obtain,

$$\hat{p}=p-\frac{1}{2}\mu_2H_0^2, \quad (97)$$

$$\hat{\zeta}=\zeta, \quad (98)$$

$$\overline{(\delta V_1)^2}=-kT\frac{\left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1}}{\left(\frac{\partial\zeta}{\partial N_1}\right)_{T,V_1}\left[\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}-\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial\mu_2}{\partial\rho_2}\right]+\left(\frac{\partial\zeta}{\partial V_1}\right)_{T,N_1}^2}, \quad (99)$$

$$\overline{(\delta N_1)^2}=kT\frac{\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}-\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial \mu_2}{\partial \rho_2}}{\left(\frac{\partial \zeta}{\partial N_1}\right)_{T,V_1}\left[\left(\frac{\partial p}{\partial V_1}\right)_{T,N_1}-\frac{1}{2}H_0^2\frac{\rho_2}{V_2}\frac{\partial \mu_2}{\partial \rho_2}\right]+\left(\frac{\partial \zeta}{\partial V_1}\right)^2_{T,N_1}}. \tag{100}$$

Note that the condition $\mu_2/\mu_1 \to 0$ imposes $H_1=0$.

We also make the following observations.

(1) The most important fact in the case of discrete systems is that the fluctuations of the intrinsic parameters of the systems depend on the magnetic permeability of its surroundings.

(2) The evaluation of fluctuations of dielectric systems can be obtained by means of the substitutions: $\mathbf{H}\to\mathbf{E}$, $\mathbf{B}\to\mathbf{D}$, $\mu\to\varepsilon$.

(3) The comments of Sec. III A 3 regarding dispersions $\overline{(\delta A)^2}$ and correlations $\overline{\delta A\ \delta B}$ apply also here.

IV. THERMODYNAMIC INEQUALITIES FOR SYSTEMS IN THE PRESENCE OF FIELDS

It is known [9], that the correlation coefficients constitute the elements of a matrix, which satisfies the following inequalities:

$$\det|C_{ab}|>0, \tag{101}$$

$$\det|C_{ab}^{-1}|>0, \tag{102}$$

where C_{ab}^{-1} denote the inverse of the matrix C_{ab}.

Equations (101) and (102) can be used to define numerous thermodynamic inequalities. In order to exemplify this possibility, we have listed in Table I inequalities that refer to a magnetizable continuum situated in a magnetoquasistatic field.

If one considers separately only two variables, X_1 and X_2, then Eq. (101) gives

$$\overline{(\delta X_1)^2}\ \overline{(\delta X_2)^2}>(\overline{\delta X_1\ \delta X_2})^2. \tag{103}$$

This kind of relations, in our opinion [9–14], resemble the well known Heisenberg's "uncertainty" relations from quantum mechanics.

Next we illustrate the relation (103) for some concrete cases.

For a magnetizable continuum in a magnetoquasistatic field, at fixed N and V, we find from Eq. (103) the following inequalities:

$$\overline{(\delta T)^2}\ \overline{(\delta B)^2}>0, \tag{104}$$

$$\overline{(\delta T)^2}\ \overline{(\delta S)^2}>k^2T^2, \tag{105}$$

$$\overline{(\delta B)^2}\ \overline{(\delta H)^2}>\frac{k^2T^2}{V^2}, \tag{106}$$

$$\overline{(\delta S)^2}\ \overline{(\delta B)^2}>k^2T^2H^2\left(\frac{\partial \mu}{\partial T}\right)^2_\rho. \tag{107}$$

For a sphere placed in a homogeneous environment (the corresponding permeabilities being μ_1 and μ_2), at fixed N and V, one obtains the relations

$$\overline{(\delta T)^2}\ \overline{(\delta B_1)^2}>0, \tag{108}$$

$$\overline{(\delta T)^2}\ \overline{(\delta S_1)^2}>k^2T^2, \tag{109}$$

$$\overline{(\delta B_1)^2}\ \overline{(\delta H_1)^2}>\frac{k^2T^2}{V_1^2}\frac{\mu_1^2}{\mu_s^2}, \tag{110}$$

$$\overline{(\delta S_1)^2}\ \overline{(\delta B_1)^2}>\frac{1}{81}k^2T^2B_1^2\mu_s'^2\left(\alpha\frac{\partial \mu_2}{\partial T}-\beta\frac{\partial \mu_1}{\partial T}\right)^2. \tag{111}$$

TABLE I. Thermodynamical inequalities.

Independent variables	Inequalities
$S,V,N,\mathbf{B}$	$[\partial(T,-\hat{p},\hat{\zeta},V\mathbf{H})/\partial(S,V,N,\mathbf{B})]>0$
$T,V,N,\mathbf{B}$	$[\partial(S,-\hat{p},\hat{\zeta},V\mathbf{H})/\partial(T,V,N,\mathbf{B})]>0$
$T,V,N,\mathbf{H}$ (X_1,X_2,X_3,X_4)	$\det\|(\partial S/\partial X_b)\delta_{1a}-(\partial\hat{p}/\partial X_a)\delta_{2b}+(\partial\hat{\zeta}/\partial X_a)\delta_{3b}+[\partial(V\mathbf{H})/\partial X_a)\cdot(\partial\mathbf{B}/\partial X_b)\|>0$
$U,V,N,\mathbf{B}$ (X_1,X_2,X_3,X_4)	$\det\|\partial T/\partial X_a\partial S/\partial X_b-(\partial\hat{p}/\partial X_a)\delta_{2b}+(\partial\hat{\zeta}/\partial X_a)\delta_{3b}+[\partial(V\mathbf{H})/\partial X_a]\delta_{4b}\|>0$
$1/T,V,N,\mathbf{B}$ (X_1,X_2,X_3,X_4)	$\det\|-T^2(\partial S/\partial X_b)\delta_{1a}-(\partial\hat{p}/\partial X_a)\delta_{2b}+(\partial\hat{\zeta}/\partial X_a)\delta_{3b}+[\partial(V\mathbf{H})/\partial X_a]\delta_{4b}\|>0$

V. SUMMARY, CONCLUSIONS, AND FINAL REMARKS

In Sec. I we presented a phenomenological theoretical approach with a view to describe fluctuations of macroscopic parameters that characterize thermodynamic systems in the presence of fields. We started with the expression of the generalized differential of the internal energy, and assume that the fluctuations involved states that are in the neighborhood of thermodynamic equilibrium.

In Sec. II we considered electromagnetic fields as a specific case. We find that the estimators of fluctuations (i.e., dispersions and correlations) depend on the different field constraints.

Discrete systems are characterized by fluctuations estimators, which are functions of intrinsic quantities of both the system and its surroundings.

In Sec. III we presented thermodynamic inequalities, which result from the fact that the correlations of the fluctuations constitute the elements of a non-negatively defined matrix. In their two-variable versions the respective inequalities can be identified as classical (nonquantum) analogs of the well known Heisenberg's ''uncertainty'' relations.

The last items from Secs. III A and III B reveal an interesting feature of Boltzmann's constant k in the following sense.

(a) The quantities $\overline{(\delta A)^2}$ and $\overline{\delta A\ \delta B}$ as fluctuation parameters are estimators of the level of stochasticity.

(b) The formulas from these sections show the fact that the respective quantities appear as products of Boltzmann's constant k with nonstochastic expressions.

(c) It follows that k can be regarded as a generic indicator of thermodynamic stochasticity.

Finally, we wish to add the following remarks. The mentioned idea regarding k was first introduced in [10]. In this work the similarity between Boltzmann's constant k and the Planck's constant $\hbar$ was revealed. In this context Planck's constant is a generic indicator of quantum stochasticity. In cases of classical (nonquantum) thermodynamical systems and quantum microparticles, k and $\hbar$ appear independently and separately. Consequently, the respective systems can be regarded as endowed with a onefold stochasticity. In the case of the quantum statistical systems k and $\hbar$ appear together in the expressions of the fluctuation parameters. This means that such systems are endowed with twofold stochasticity (for more details see Ref. [10]).

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APPENDIX: PROOF OF THE RELATION (15)

We consider the second order approximation in terms of the fluctuations δX_a of the corresponding independent variables ($X_a = T,V,N,\mathbf{B}$). Then for the quantities $\delta\hat{U}$ and δS one obtains,

$$\begin{aligned}\delta\hat{U} = {} & \left(\frac{\partial\hat{U}}{\partial T}\right)_{V,N,\mathbf{B}}\delta T + \left(\frac{\partial\hat{U}}{\partial V}\right)_{T,N,\mathbf{B}}\delta V + \left(\frac{\partial\hat{U}}{\partial N}\right)_{T,V,\mathbf{B}}\delta N \\ & + \left(\frac{\partial\hat{U}}{\partial\mathbf{B}}\right)_{T,V,N}\cdot\delta\mathbf{B} + \frac{1}{2}\left(\frac{\partial^2\hat{U}}{\partial T^2}\right)_{V,N,\mathbf{B}}(\delta T)^2 \\ & + \frac{1}{2}\left(\frac{\partial^2\hat{U}}{\partial V^2}\right)_{T,N,\mathbf{B}}(\delta V)^2 + \frac{1}{2}\left(\frac{\partial^2\hat{U}}{\partial N^2}\right)_{T,V,\mathbf{B}}(\delta N)^2 \\ & + \frac{1}{2}\left(\frac{\partial^2\hat{U}}{\partial B^2}\right)_{T,V,N}(\delta B)^2 + \frac{\partial^2\hat{U}}{\partial V\,\partial T}\delta V\,\delta T + \frac{\partial^2\hat{U}}{\partial N\,\partial T}\delta N\,\delta T \\ & + \frac{\partial^2\hat{U}}{\partial B\,\partial T}\delta B\,\delta T + \frac{\partial^2\hat{U}}{\partial V\,\partial N}\delta V\,\delta N + \frac{\partial^2\hat{U}}{\partial V\,\partial B}\delta V\,\delta B \\ & + \frac{\partial^2\hat{U}}{\partial N\,\partial B}\delta N\,\delta B,\end{aligned} \tag{A1}$$

$$\begin{aligned}\delta S = {} & \left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}\delta T + \left(\frac{\partial S}{\partial V}\right)_{T,N,\mathbf{B}}\delta V + \left(\frac{\partial S}{\partial N}\right)_{T,V,\mathbf{B}}\delta N \\ & + \left(\frac{\partial S}{\partial B}\right)_{T,V,N}\delta B + \frac{1}{2}\left(\frac{\partial^2 S}{\partial T^2}\right)_{V,N,\mathbf{B}}(\delta T)^2 \\ & + \frac{1}{2}\left(\frac{\partial^2 S}{\partial V^2}\right)_{T,N,\mathbf{B}}(\delta V)^2 + \frac{1}{2}\left(\frac{\partial^2 S}{\partial N^2}\right)_{T,V,\mathbf{B}}(\delta N)^2 \\ & + \frac{1}{2}\left(\frac{\partial^2 S}{\partial B^2}\right)_{T,V,N}(\delta B)^2 + \frac{\partial^2 S}{\partial V\,\partial T}\delta V\,\delta T + \frac{\partial^2 S}{\partial N\,\partial T}\delta N\,\delta T \\ & + \frac{\partial^2 S}{\partial B\,\partial T}\delta B\,\delta T + \frac{\partial^2 S}{\partial V\,\partial N}\delta V\,\delta N + \frac{\partial^2 S}{\partial V\,\partial B}\delta V\,\delta B \\ & + \frac{\partial^2 S}{\partial N\,\partial B}\delta N\,\delta B,\end{aligned} \tag{A2}$$

where

$$\left(\frac{\partial\hat{U}}{\partial T}\right)_{V,N,\mathbf{B}} = T\left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}, \tag{A3}$$

$$\left(\frac{\partial\hat{U}}{\partial V}\right)_{T,N,\mathbf{B}} = T\left(\frac{\partial S}{\partial V}\right)_{T,N,\mathbf{B}} - \hat{p}, \tag{A4}$$

$$\left(\frac{\partial\hat{U}}{\partial N}\right)_{T,V,\mathbf{B}} = T\left(\frac{\partial S}{\partial N}\right)_{T,V,\mathbf{B}} + \hat{\zeta}, \tag{A5}$$

$$\left(\frac{\partial\hat{U}}{\partial B}\right)_{T,V,N} = T\left(\frac{\partial S}{\partial B}\right)_{T,V,N} + V\mathbf{H}, \tag{A6}$$

$$\left(\frac{\partial^2 \hat{U}}{\partial T^2}\right)_{V,N,\mathbf{B}} = T\left(\frac{\partial^2 S}{\partial T^2}\right)_{V,N,\mathbf{B}} + \left(\frac{\partial S}{\partial T}\right)_{V,N,\mathbf{B}}, \quad \text{(A7)}$$

$$\left(\frac{\partial^2 \hat{U}}{\partial V^2}\right)_{T,N,\mathbf{B}} = T\left(\frac{\partial^2 S}{\partial V^2}\right)_{T,N,\mathbf{B}} - \left(\frac{\partial \hat{p}}{\partial V}\right)_{T,N,\mathbf{B}}, \quad \text{(A8)}$$

$$\left(\frac{\partial^2 \hat{U}}{\partial N^2}\right)_{T,V,\mathbf{B}} = T\left(\frac{\partial^2 S}{\partial N^2}\right)_{T,V,\mathbf{B}} + \left(\frac{\partial \hat{\zeta}}{\partial N}\right)_{T,V,\mathbf{B}}, \quad \text{(A9)}$$

$$\left(\frac{\partial^2 \hat{U}}{\partial B^2}\right)_{V,N,\mathbf{B}} = T\left(\frac{\partial^2 S}{\partial B^2}\right)_{V,N,\mathbf{B}} + V\left(\frac{\partial H}{\partial B}\right)_{V,N,\mathbf{B}}, \quad \text{(A10)}$$

$$\frac{\partial^2 \hat{U}}{\partial V\,\partial T} = T\frac{\partial^2 S}{\partial V\,\partial T}; \quad \frac{\partial^2 \hat{U}}{\partial N\,\partial T} = T\frac{\partial^2 S}{\partial N\,\partial T}; \quad \frac{\partial^2 \hat{U}}{\partial B\,\partial T} = T\frac{\partial^2 S}{\partial B\,\partial T}, \quad \text{(A11)}$$

$$\frac{\partial^2 \hat{U}}{\partial V\,\partial N} = T\frac{\partial^2 S}{\partial V\,\partial N} + \left(\frac{\partial \hat{\zeta}}{\partial V}\right)_{T,N,\mathbf{B}}, \quad \text{(A12)}$$

$$\frac{\partial^2 \hat{U}}{\partial V\,\partial B} = T\frac{\partial^2 S}{\partial V\,\partial B} + \left(\frac{\partial (VH)}{\partial V}\right)_{T,N,\mathbf{B}}, \quad \text{(A13)}$$

$$\frac{\partial^2 \hat{U}}{\partial N\,\partial B} = T\frac{\partial^2 S}{\partial N\,\partial B} + V\left(\frac{\partial H}{\partial N}\right)_{T,V,\mathbf{B}}. \quad \text{(A14)}$$

The above Eqs. (A1)–(A14) in conjunction with Eqs. (1), (2), and (14) give directly the relation (15).

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